DONOR BEHAVIOR IN INDIUM-ALLOYED SILICON*

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The anomalous doping behavior of Si regrown from In solution was studied by (1) Schottky barrier evaluation of conductivity type, (2) electron microprobe analysis for phosphorus, and (3) channeling effect measurements for interstitial In. The latter showed In present at $\sim 10^{19}$ cm^{-3}, but not occupying a regular substitutional or interstitial position. A correlation was found in the first two measurements between phosphorus contamination and *n*-type conductivity. When the In was contacted only by quartz freshly etched in HF, the *n*-type behavior and phosphorus contamination disappeared. The anomalous doping behavior is most likely due to phosphorus inpurity picked up by the In.

Indium introduced into Si during Czochralski crystal growth or by diffusion is a conventional substitutional acceptor. However, when In is implanted or alloyed into Si, an anomalous doping behavior results. Channeling effect measurements[1] have shown that both In and Tl implantations yield an interstitial component. Indeed Tl-implanted Si even turns out to be *n*-type in electrical measurements.[2] Furthermore, Si recrystallized from In solution, i.e., "In-alloyed" Si, is also reported[3] to exhibit *n*-type behavior, contrary to the previously mentioned acceptor behavior.[4]

The present experiments were undertaken to determine the origin of the *n*-type behavior in In-alloyed Si. Our results indicate that the donor behavior is associated with the presence of phosphorus impurity, rather than with interstitial In as has been proposed.[3]

Both *n*- and *p*-type Si substrates were used for the present alloy studies. The *n*-type substrates were 0.2 Ω-cm and the *p*-type 0.3 Ω-cm. The In used was in the form of high-purity rods (Asarco, grade A-58), which emission spectroscopy showed to contain 2 ppm Cd and 1 ppm Sn, with other metallic impurities at concentrations less than 1 ppm or not detected. Phosphorus concentration was reportedly[5] less than 0.1 ppm.

Pellets of In 0.3—0.4 mm in diameter were cut from the In rod, the In being contacted only by razor blades and microscope slides. The pellets were placed between two Si dice held 0.2 mm apart by a quartz spacer. This assembly was heated to ~ 950 °C in high-purity He and held at this temperature for about 10 min to cause the In to wet and dissolve the Si. The assembly was then rapidly cooled, to facilitate any kinetic effects on In solubility, reaching the melting point of In, 156 °C, in about 10 sec. The In was removed in HCl. Regions where Si had been dissolved and then regrown could be seen wherever an In pellet had been located.

Electrical evaluation of the regrowth regions was obtained from current-voltage characteristics of Schottky barriers, formed by evaporating Au dots 75 μ in diameter onto specimens freshly treated in HF. The *I-V* characteristics were not uniform from dot to dot on a given Si die. However, an appreciable fraction, up to one-half in favorable cases, of Ohmic contacts were observed, i.e., *I-V*'s linear to 1 V or more and with slopes of 100 Ω or less. These Ohmic contacts were used to characterize the underlying regrowth regions as being of the same conductivity type as the substrate.

Specimens treated as described above were found to be predominantly *n* type, in agreement with the results reported by Migitaki.[3] An estimation of the carrier concentration from the *I-V* characteristics indicated concentrations of the order of 5×10^{18} or 10^{19} cm^{-3}. Electron microprobe measurements on the specimen exhibiting the most Ohmic contacts to an *n*-type substrate, as described above, are shown in Fig. 1(a) and give clear evidence for phosphorus concentrations approximating the electron concentrations. This

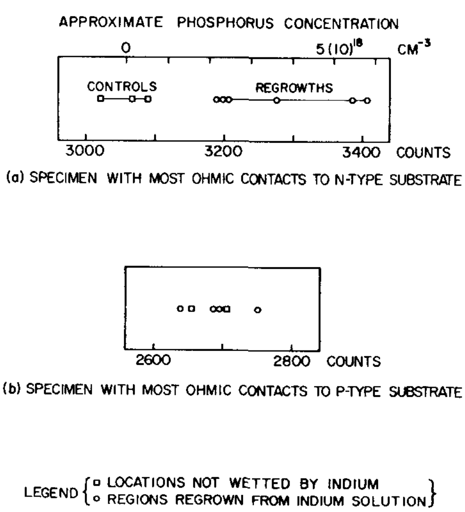

FIG. 1. Electron microprobe counts, taken from the phosphorus K_α line with an ADP crystal, for various locations in two Si specimens. In the case of each specimen, the same quantity of charge was incident for all locations. Phosphorus concentrations are estimated from counts taken on a GaP specimen. Control specimens were used to estimate background counts.

suggested that the n-type behavior was due to phosphorus impurity rather than to interstitially trapped In, as previously proposed.[3]

Channeling effect measurements with 1.2- and 1.56-MeV ^{4}He ions along $\langle 111\rangle$ and random orientations were made on similar samples. The data indicated an In concentration of 1 to 2×10^{19} cm^{-3} averaged over an area of ~ 1.5 mm^2. In the energy spectra of the backscattered particles, the depth distribution of In could be determined to depths of about 6000–8000 Å depending on energy of the analysis beam. Over these depths the In concentration did not show an appreciable decrease. The sample was reexamined after a light etch estimated to have removed several microns of Si. A somewhat lower concentration of In was found. The scattering yield from In in $\langle 111\rangle$ and random orientations were the same within statistical error, indicating that the In atoms were displaced off any regular substitutional or interstitial lattice sites. From these measurements one can estimate that any interstitial would be at concentrations less than ~ 2×10^{18} cm^{-3}, i.e., below the electron concentration observed. Since these channeling measurements were made over an area of ~ 1.5 mm^2, there is the possibility that the In detected may have been present as one or more localized aggregates.

At this point, two explanations remained possible for the anomalous n-type behavior of In-alloyed Si: (1) phosphorus picked up during handling or (2) entrapped In, even though not located at a regular interstitial site. The first possibility was pursued, as a variety of cleaner handling procedures could readily be tested. Since In is known to be an effective scavenger of surface impurities with which it comes into contact, due to its wetting action, various tools for handling the In were tried. Regrowths were formed, as previously described, and the fraction of Ohmic contacts to p- and n-type substrates measured. In terms of these electrical evaluations, best results were obtained when the In was contacted only by quartz that had been freshly etched in HF. Electrical measurements on n- and p-type samples prepared with such stringent precaution and with the same temperature history as previously described indicated a large fraction of Ohmic contacts to p-type Si but not to n-type Si. In no case was there evidence for an n^+ region. Electron microprobe measurements were made on the specimen, with p-type substrate, exhibiting the largest fraction of Ohmic contacts as defined above. The results, as shown in Fig. 1(b), gave no positive indication of phosphorus, i.e., the phosphorus concentration was approximately or less than 10^{18} cm^{-3}.

The effectiveness, thus shown, of phosphorus contamination in overruling the intrinsic doping effect of In in Si raises interesting questions about the distribution coefficient k_p in this system. It is planned to measure k_p in another study now underway. It also should be mentioned that the present results suggest an explanation for the well-known effectiveness of In solder in making Ohmic contacts to n-type Si. The usual rules[6] for Schottky barrier heights on Si would predict too high a barrier for Ohmic contact between n-type Si and In at 300 °K. However, any n^+ regions would serve effectively as Ohmic contacts.

In conclusion, the present evidence indicates that the n-type behavior observed in In-alloyed Si, at least for temperatures $\lesssim$ 900 °C, is associated with the presence of phosphorus contamination rather than with interstitial In.

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[1]L. Eriksson, J.A. Davies, N.G.E. Johansson, and J.W. Mayer J. Appl. Phys. 40, 842 (1969).

[2]R. Baron, G.A. Shifrin, O.J. Marsh, and J.W. Mayer, J. Appl. Phys. 40, 3702 (1970).

[3]Masatoshi Migitaka, J. Appl. Phys. 36, 2139 (1965).

[4]This last result is somewhat unexpected in that other column III metals, e.g., Al which is commonly used with Si, show acceptor behavior during alloying the same as in crystal growth. See, for example, Richard A. Gudmundsen and J. Maserjian, Jr., J. Appl. Phys. 28, 1308 (1957).

[5]S.C. Carapella, Jr. (private communication).

[6]C.A. Mead, Solid-State Electron. 9, 1023 (1966).